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SYNTHESIS AND THERMAL CURING OF POLY(ENAMINONITRILES)
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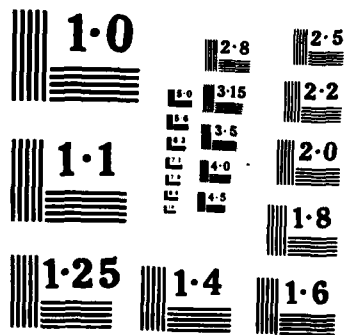
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"Synthesis and Thermal Curing of Poly(enaminonitriles)"

by

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Submitted to
Macromolecules

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ABSTRACT

A thermally stable poly(enaminonitrile) has been synthesized by vinylic nucleophilic substitution polymerization. The polymer does not lose mass below 446°, and retains >70% of its original mass at 900° (by TGA in nitrogen). Evidence is presented for an unprecedented curing reaction which does not involve the emission of volatile by-products.



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Synthesis and Curing of a Thermally Stable Poly(enaminonitrile).¹

Most thermally stable organic polymers are difficult to process because they possess very high transition temperatures and/or poor solubility. Therefore, research has centered on the synthesis of tractable polymers which are later cured to a thermally stable form. Polyimides are a well-known example of this approach.² A disadvantage of this method is that the curing reaction generally releases a small molecule (often H₂O), which can cause pinholes and structural defects in the bulk material. To address this problem, we are studying a class of thermally stable polymers which, preliminary data indicate, cures by a rearrangement reaction, without the formation of volatile by-products.

Earlier work on poly(enaminoesters)³ led us to consider analogous poly(enaminonitriles). Poly(enaminoesters) undergo the Conrad-Limpach cyclization⁴ to form poly(4-quinolones) with the concomitant expulsion of alcohol. Similarly, poly(enaminonitriles) might be induced to cure by an intramolecular Hoesch reaction⁵ at high temperature to produce poly(4-aminoquinolines) (Scheme I).

The poly(enaminonitrile) 1 was synthesized by vinylic nucleophilic substitution,⁶⁻⁸ a reaction which is known to proceed rapidly and with few side reactions. Previous work^{8,9} had demonstrated that aromatic amines reacted smoothly with α -halo- β,β -dicyanoethylenes to produce enamines. Therefore, we developed a synthesis of 1,4-bis(α -chloro- β,β -dicyanovinyl)benzene monomer (2), as follows: Two moles of malononitrile were condensed with terephthaloyl chloride under base-catalyzed, phase-transfer conditions. The resulting disodium bisenolate 3 was reacted with phosphorous oxychloride in dry methylene chloride to form the desired monomer 2 (Scheme II).

Polymerization was carried out by heating equimolar amounts of monomer 2 and 4,4'-diaminodiphenyl ether in *N*-methylpyrrolidone under nitrogen at 70° for 16 hours. 4-(Dimethylamino)pyridine was used as the acid acceptor (Scheme III). The polymer was isolated by precipitation into water, then purified by repeated reprecipitation from *N,N*-dimethylformamide (DMF) into methanol. After drying in vacuo at 100°, a 65% yield of polymer 1 was produced. An intrinsic viscosity (measured at 25° in DMF) as high as 0.84 dL/g was readily obtained. The polymer 1 was greenish yellow, soluble in polar aprotic solvents, and formed very tough (fingernail creasable), transparent films when cast from DMF. IR and NMR spectra of the polymer corresponded well with those obtained for the analogous model compound 4 (Figures 1 and 2).

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The poly(enaminonitrile) obtained in this way exhibited excellent thermal stability. Thermogravimetric analysis of 1 (Perkin-Elmer TGA 7 System) in nitrogen with heating at 10°/min revealed an initial mass loss at 446°; greater than 70% of the polymer's original mass was retained at 900° (Figure 3). Isothermal aging studies done in nitrogen for 12 hours at 400° and 500° showed very slow mass loss after an initial small evolution of lighter molecules from the sample (Figure 4).

Samples of polymer 1 heated above 350° under nitrogen became orange and were insoluble in solvents for the untreated polymer. The IR spectrum of the cured polymer displayed a loss of the enamine N-H stretching band at 3200 cm^{-1} and a decrease in the intensity of the $\text{C}\equiv\text{N}$ band at 2205 cm^{-1} . At the same time, two bands at 3450 and 3500 cm^{-1} appeared (Figure 5). These spectral features are consistent with rearrangement, at least in part, of the enaminonitrile repeat unit into a

4-aminoquinoline.

Differential scanning calorimetry (Perkin Elmer DSC 7 System) of the poly(enaminonitrile) was conducted under nitrogen using a 20°/min heating rate. During the initial scan, a T_g at 195° and a broad exotherm near 360° were detected. These features did not recur when the sample was cooled and reheated (Figure 6).

The results of a model reaction provided additional evidence for the formation of 4-aminoquinoline from enaminonitrile upon thermolysis. When 3-phenyl-3-(phenylamino)-2-propenenitrile (5) was heated at 650° under flash thermolysis conditions, 4-amino-2-phenylquinoline (6) was obtained in 30% yield (Scheme IV).^{9,10}

In conclusion, a polymer with excellent thermal stability has been synthesized, which may be cured without the emission of volatile fragments. We believe that the remarkable properties of this polymer will permit its application as a component of ablative coatings, composite materials, and as an interlayer dielectric for integrated circuit fabrication.

We are currently studying the curing reaction, as well as synthesizing similar monomers and employing a variety of comonomers to produce other poly(enaminonitriles).

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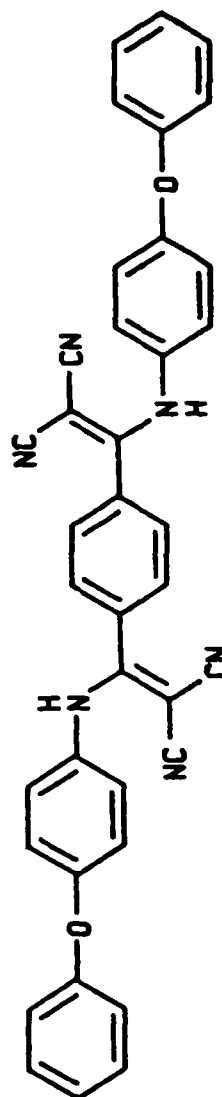


FIGURE AND SCHEME CAPTIONS

Figure 1. Comparison of IR spectra of poly(enaminonitrile) 1 (upper, obtained from a film of the polymer) and that of the analogous model compound 4 (lower, obtained as a KBr pellet).

Figure 2. Comparison of ^{13}C NMR spectra of poly(enaminonitrile) 1 (upper) and that of the analogous model compound 4 (lower), measured at 25.1 MHz in $((\text{CD}_3)_2\text{SO})$ at 20° .

Figure 3. TGA of poly(enaminonitrile) 1 in nitrogen (solid line) and in air (dashed line). A $10^\circ/\text{min}$ heating rate was used.

Figure 4. Isothermal aging thermograms of poly(enaminonitrile) 1 in nitrogen at 400° (solid line) and at 500° (dashed line).

Figure 5. IR spectra of poly(enaminonitrile) 1 after heat-curing at 400° under nitrogen for (starting from the top) 0 hour, 1 hour, 2 hours, and 4 hours.

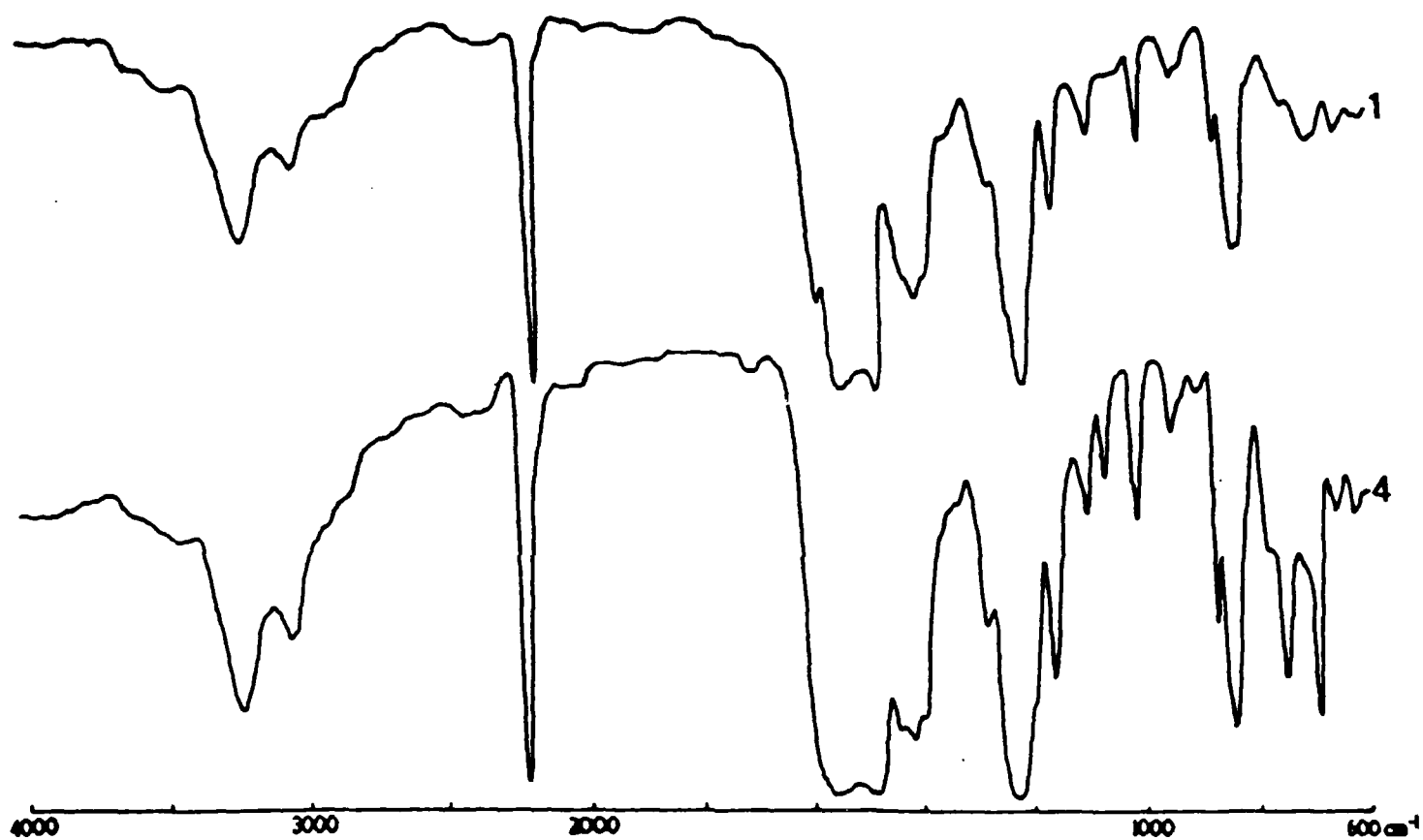
Figure 6. DSC of poly(enaminonitrile) 1 in nitrogen using a $20^\circ/\text{min}$ heating rate. The initial scan is shown as a solid line; the repeated scan as a dashed line.

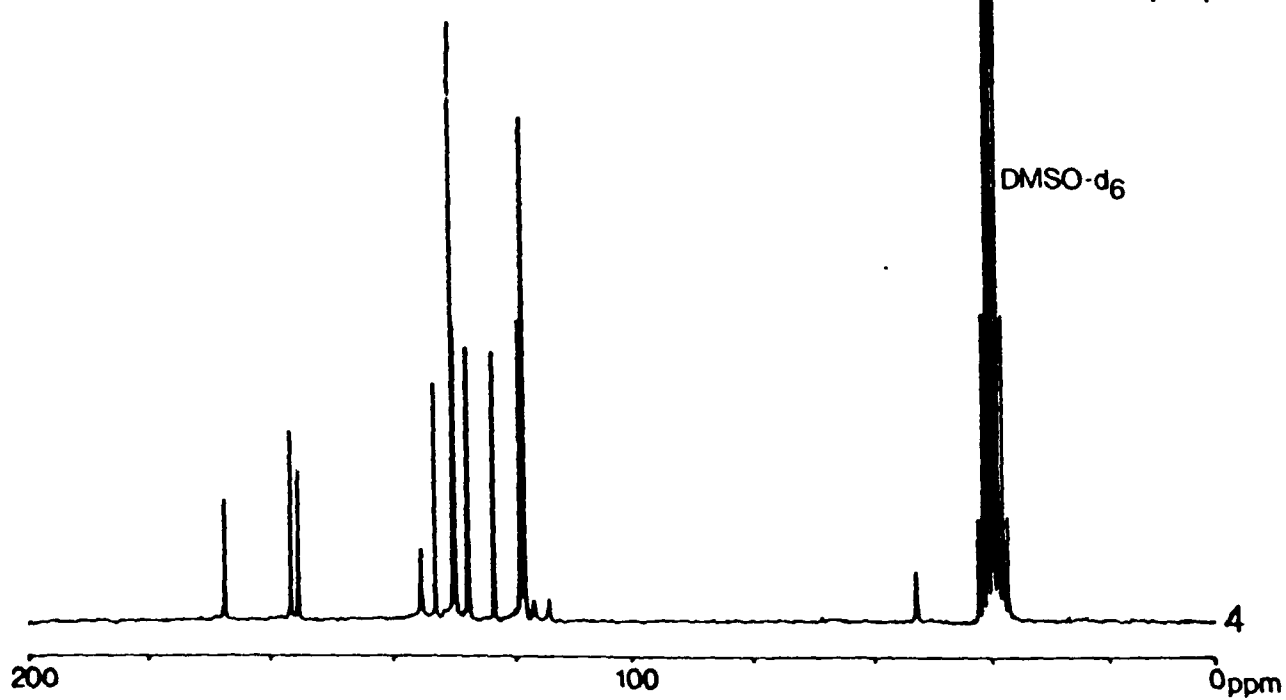
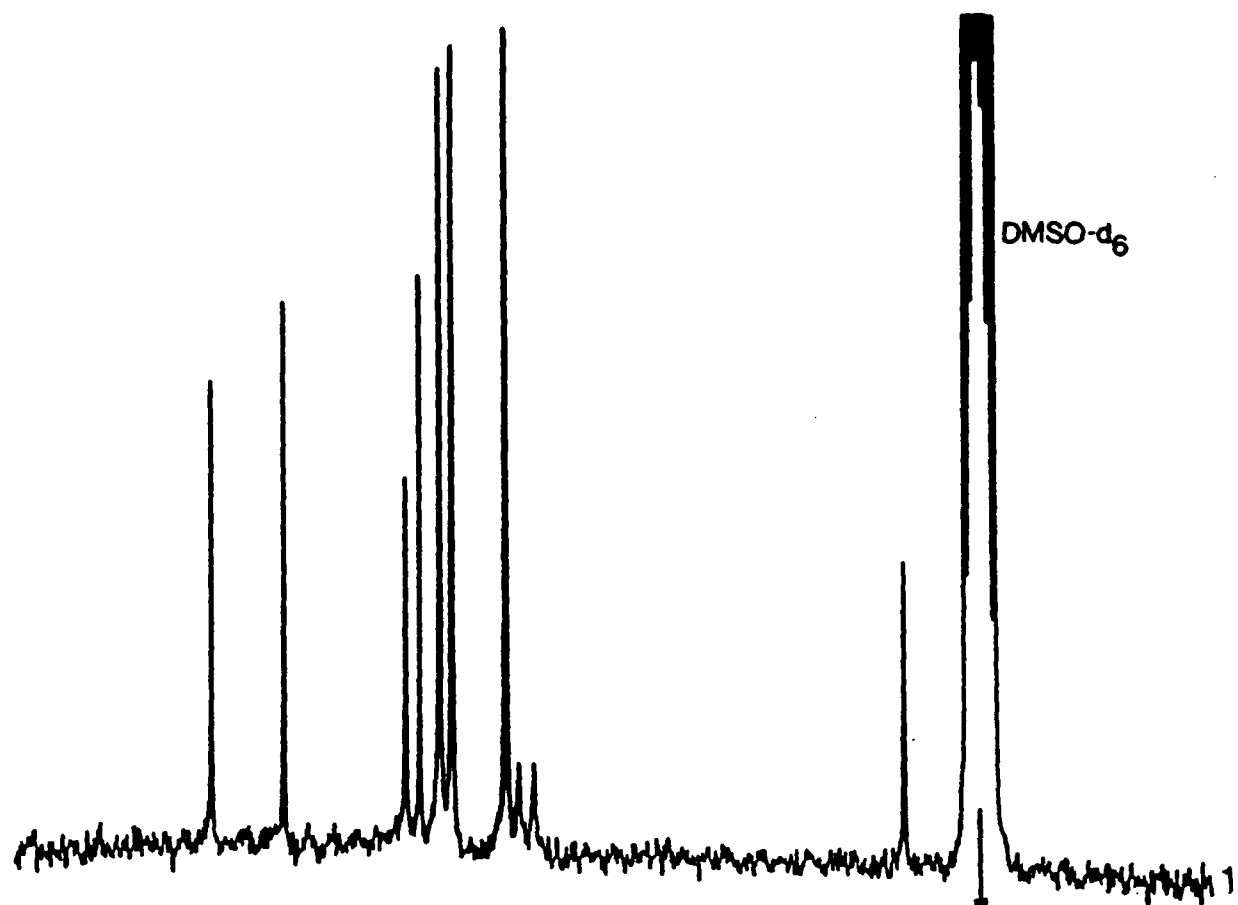
Scheme I. Comparison of the curing reactions of poly(enaminoesters) and poly(enaminonitriles).

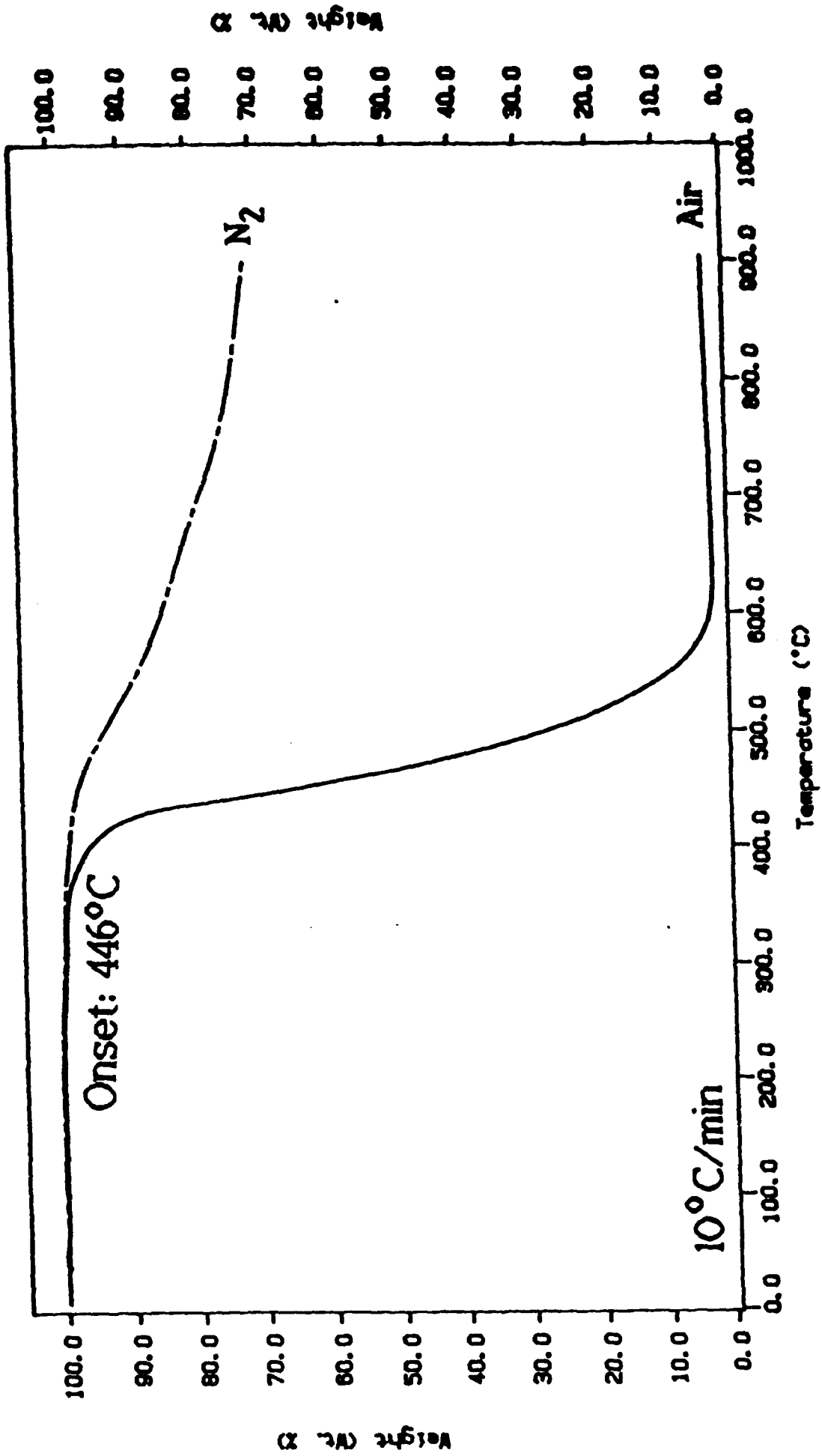
Scheme II. Synthesis of 1,4-bis(α -chloro- β,β -dicyanovinyl)benzene monomer (2).

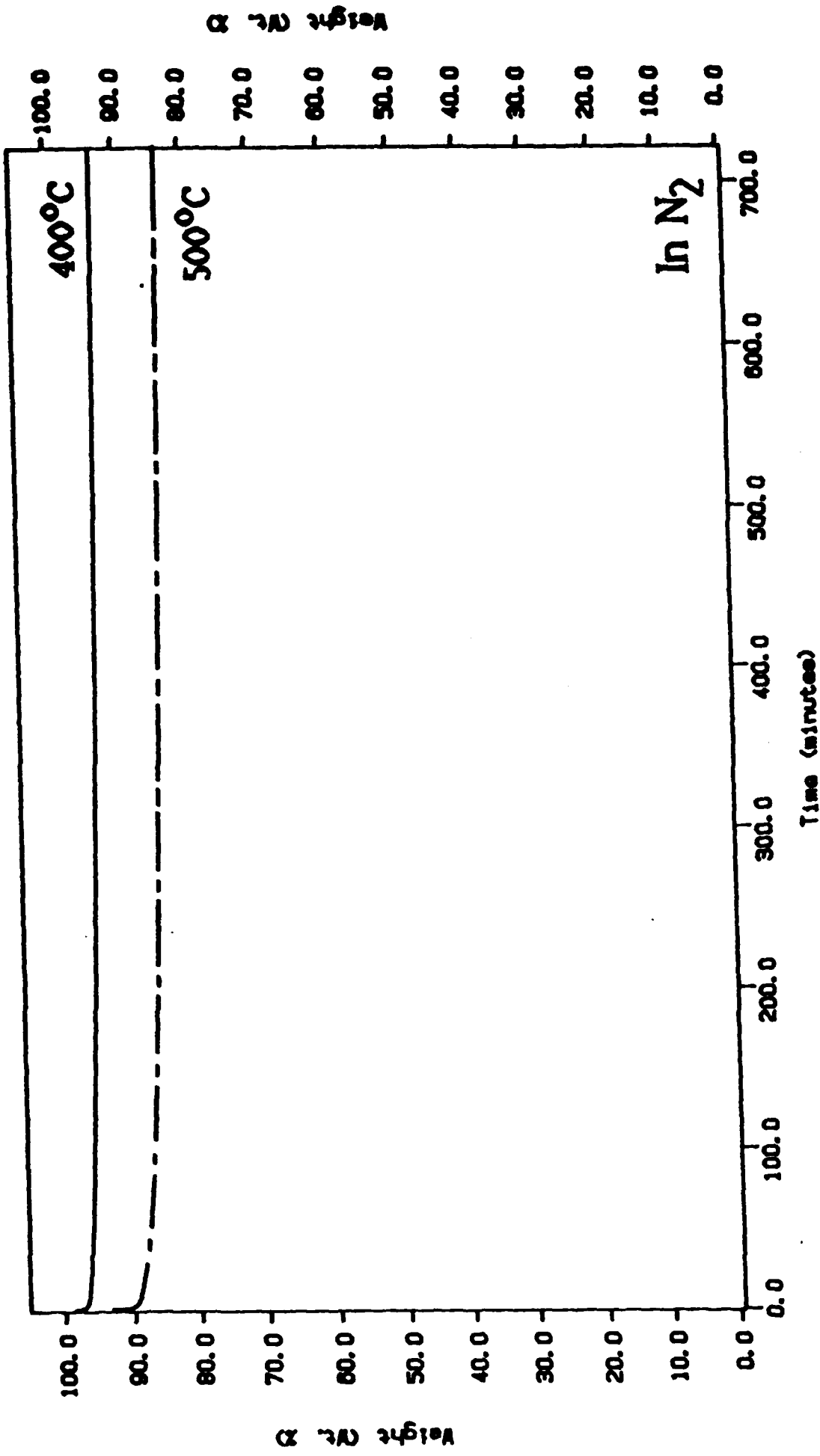
Scheme III. Polymerization of 1,4-bis(α -chloro- β,β -dicyanovinyl)benzene (2) with 4,4'-diaminodiphenyl ether.

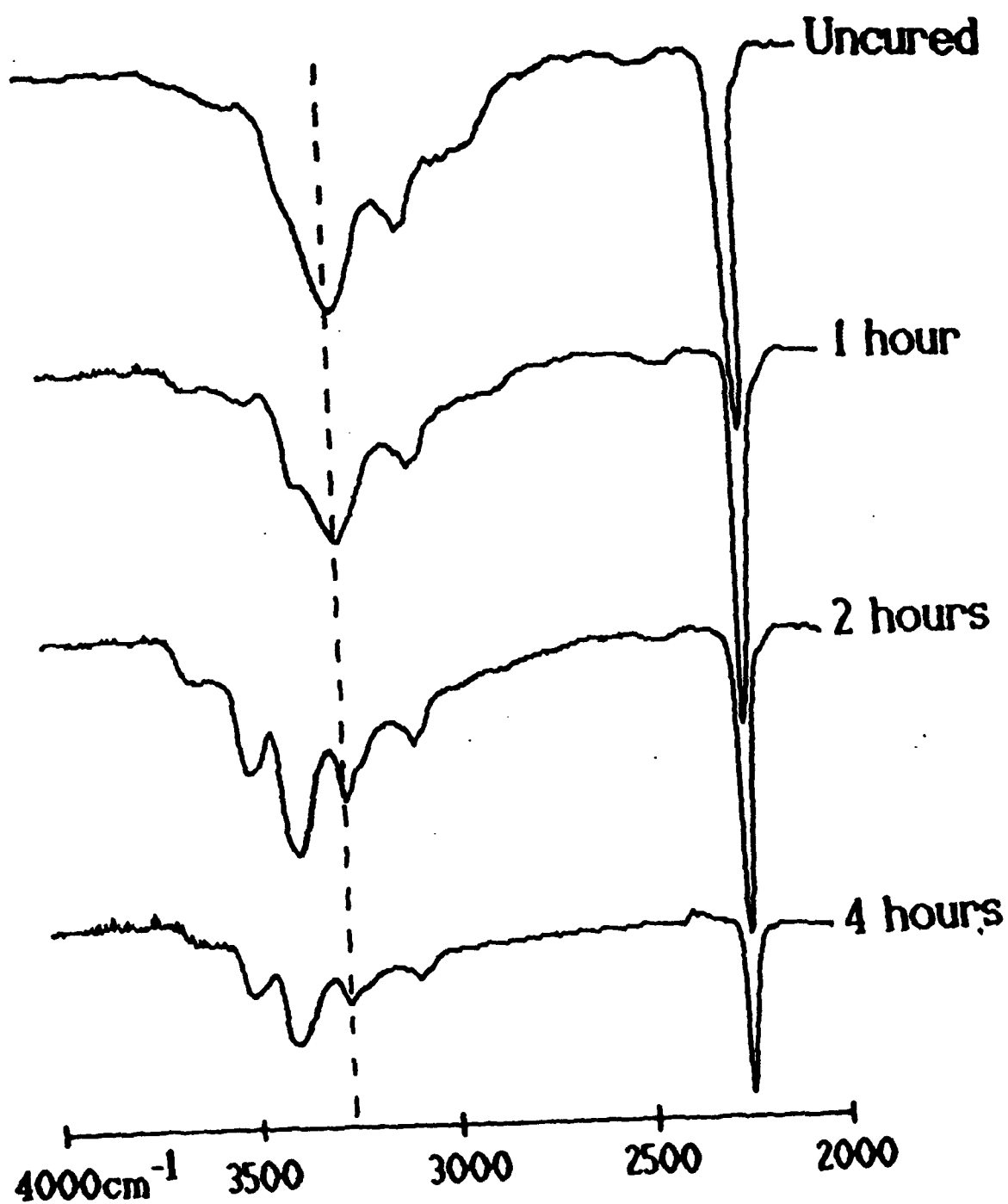
Scheme IV. Synthesis of 4-amino-2-phenylquinoline (6) by flash vacuum thermolysis.

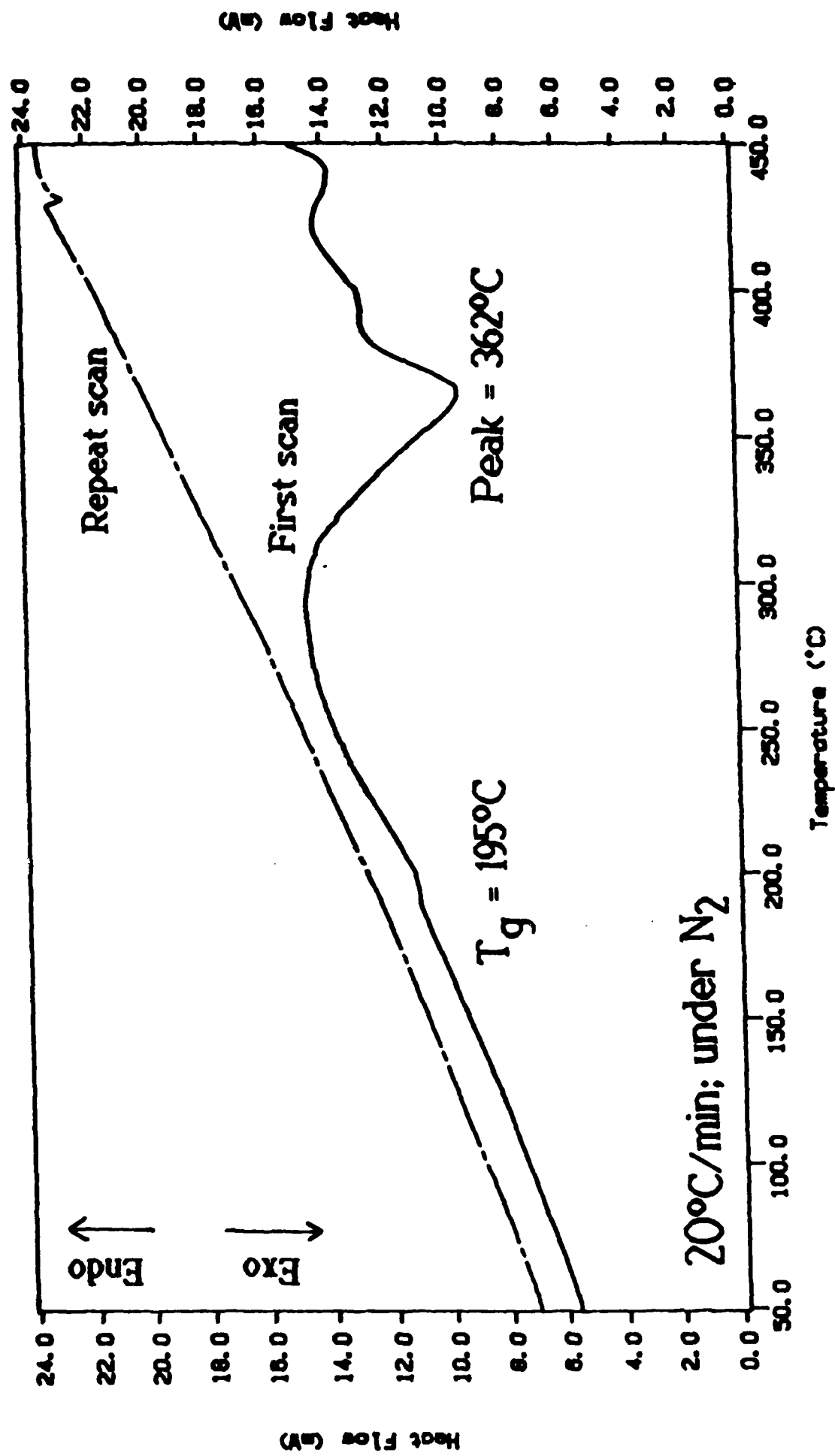


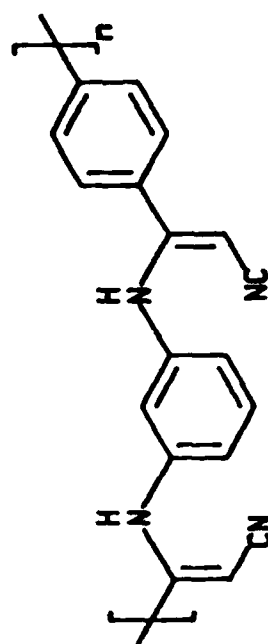
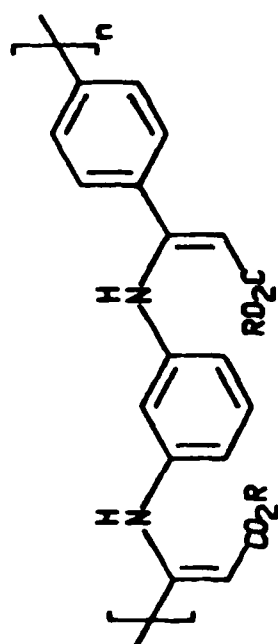
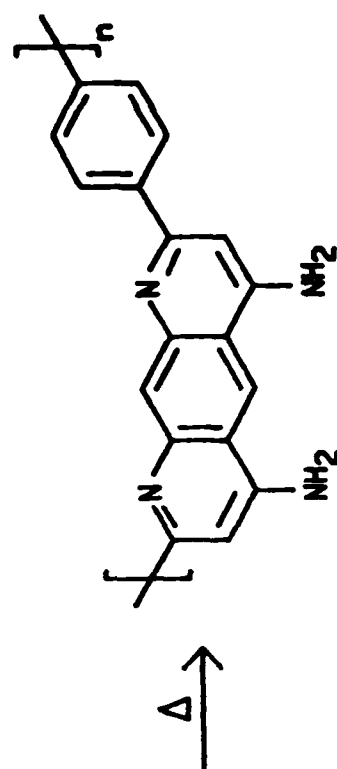
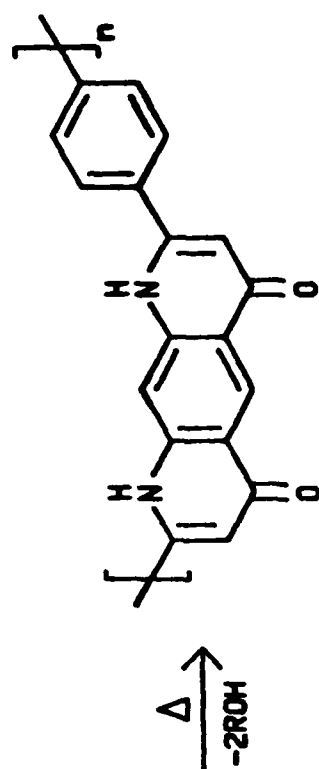


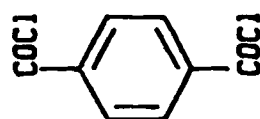
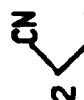
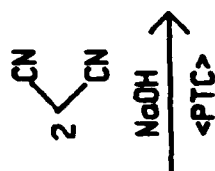
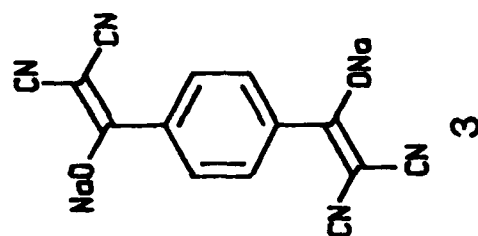
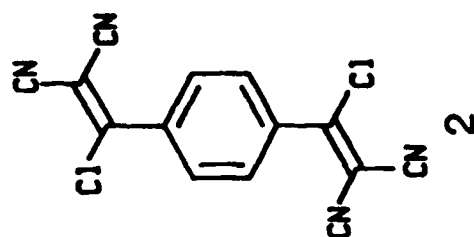


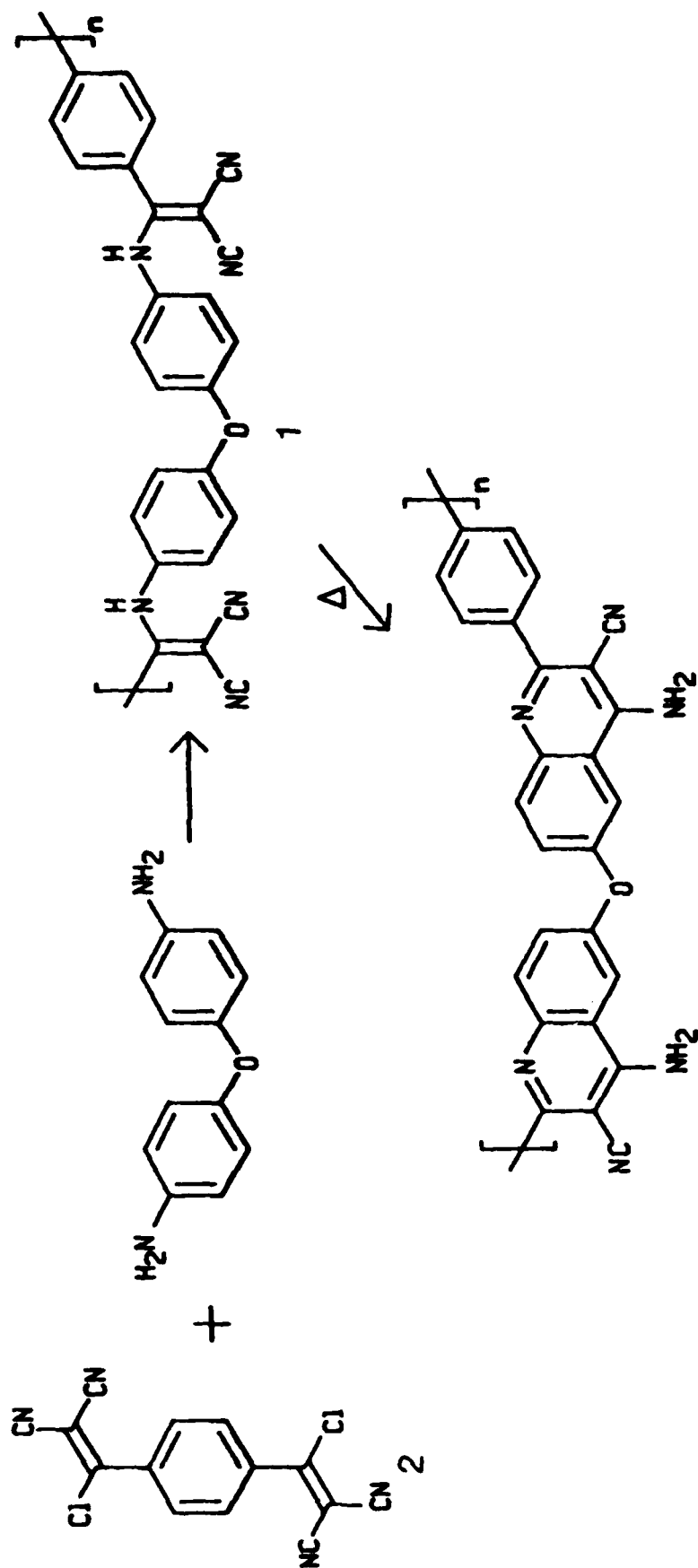


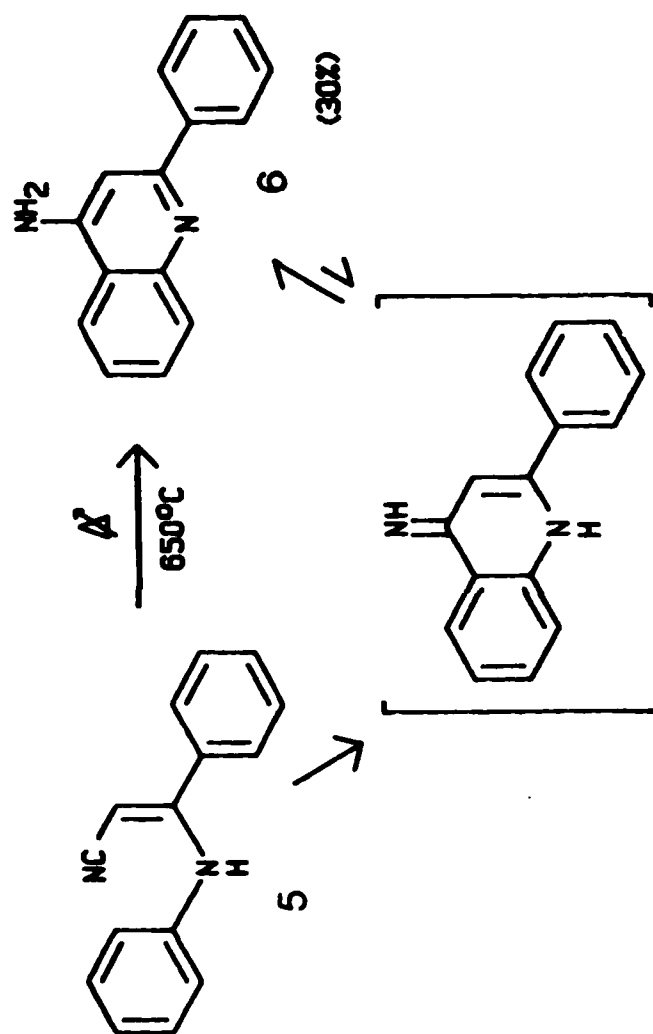












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